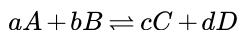# 13.3: The Equilibrium Constant

> 🧠 **Learning Objectives**
>
> - Explain the importance of the equilibrium constant.
> - Construct an equilibrium constant expression for a chemical reaction.

In the mid 1860s, Norwegian scientists C. M. Guldberg and P. Waage noted a peculiar relationship between the amounts of reactants and products in an equilibrium. No matter how many reactants they started with, a certain ratio of reactants and products was achieved at equilibrium. Today, we call this observation the **law of mass action**. It relates the amounts of reactants and products at equilibrium for a chemical reaction. For a general chemical reaction occurring in solution,

$$aA + bB \rightleftharpoons cC + dD$$

the **equilibrium constant**, also known as K_{eq}, is defined by the following expression:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where [A] is the molar concentration of species A at equilibrium, and so forth. The coefficients a, b, c, and d in the chemical equation become exponents in the expression for K_{eq}. The K_{eq} is a characteristic numerical value for a given reaction at a given temperature; that is, each chemical reaction has its own characteristic K_{eq}. The concentration of each reactant and product in a chemical reaction at equilibrium is *related*; the concentrations cannot be random values, but they depend on each other. The numerator of the expression for K_{eq} has the concentrations of every product (however many products there are), while the denominator of the expression for K_{eq} has the concentrations of every reactant, leading to the common *products over reactants* definition for the K_{eq}.

Let us consider a simple example. Suppose we have this equilibrium:

$$A \rightleftharpoons B$$

There is one reactant, one product, and the coefficients on each are just 1 (assumed, not written). The K_{eq} expression for this equilibrium is

$$K_{eq} = \frac{[B]}{[A]}$$

(Exponents of 1 on each concentration are understood.) Suppose the numerical value of K_{eq} for this chemical reaction is 2.0. If [B] = 4.0 M, then [A] must equal 2.0 M so that the value of the fraction equals 2.0:

$$K_{eq} = \frac{[B]}{[A]} = \frac{4.0}{2.0} = 2.0$$

By convention, the units are understood to be M and are omitted from the K_{eq} expression. Suppose [B] were 6.0 M. For the K_{eq} value to remain constant (it is, after all, called the equilibrium *constant*), then [A] would have to be 3.0 M at equilibrium:

$$K_{eq} = \frac{[B]}{[A]} = \frac{6.0}{3.0} = 2.0$$

If [A] were *not* equal to 3.0 M, the reaction would not be at equilibrium, and a net reaction would occur until that ratio was indeed 2.0. At that point, the reaction is at equilibrium, and any net change would cease. (Recall, however, that the forward and reverse reactions do not stop because chemical equilibrium is dynamic.)

The issue is the same with more complex expressions for the K_{eq}; only the mathematics become more complex. Generally speaking, given a value for the K_{eq} and all but one concentration at equilibrium, the missing concentration can be calculated.

✔ Example 13.3.1

Given the following reaction:

$$H_2 + I_2 \rightleftharpoons 2\,HI \tag{13.3.1}$$

If the equilibrium [HI] is 0.75 M and the equilibrium [H_2] is 0.20 M, what is the equilibrium [I_2] if the K_{eq} is 0.40?

Solution

We start by writing the K_{eq} expression. Using the *products over reactants* approach, the K_{eq} expression is as follows:

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

Note that [HI] is squared because of the coefficient 2 in the balanced chemical equation. Substituting for the equilibrium [H_2] and [HI] and for the given value of K_{eq}:

$$0.40 = \frac{(0.75)^2}{(0.20)[I_2]}$$

To solve for [I_2], we have to do some algebraic rearrangement: divide the 0.40 into both sides of the equation and multiply both sides of the equation by [I_2]. This brings [I_2] into the numerator of the left side and the 0.40 into the denominator of the right side:

$$[I_2] = \frac{(0.75)^2}{(0.20)(0.40)}$$

Solving,

[I_2] = 7.0 M

The concentration unit is assumed to be molarity. This value for [I_2] can be easily verified by substituting 0.75, 0.20, and 7.0 into the expression for K_{eq} and evaluating: you should get 0.40, the numerical value of K_{eq} (and you do).

? Exercise 13.3.1

Given the following reaction:

$$H_2 + I_2 \rightleftharpoons 2\,HI \tag{13.3.2}$$

If the equilibrium [HI] is 0.060 M and the equilibrium [I_2] is 0.90 M, what is the equilibrium [H_2] if the K_{eq} is 0.40?

Answer

0.010 M

In some types of equilibrium problems, square roots, cube roots, or even higher roots need to be analyzed to determine a final answer. Make sure you know how to perform such operations on your calculator; if you do not know, ask your instructor for assistance.

✔ Example 13.3.2

The following reaction is at equilibrium:

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 \tag{13.3.3}$$

The K_{eq} at a particular temperature is 13.7. If the equilibrium [N_2] is 1.88 M and the equilibrium [NH_3] is 6.62 M, what is the equilibrium [H_2]?

Solution

We start by writing the K_{eq} expression from the balanced chemical equation:

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Substituting for the known equilibrium concentrations and the K_{eq}, this becomes

$$13.7 = \frac{(6.62)^2}{(1.88)[H_2]^3}$$

Rearranging algebraically and then evaluating the numerical expression, we get

$$[H_2]^3 = \frac{(6.62)^2}{(1.88)(13.7)} = 1.7015219754$$

To solve for [H2], we need to take the cube root of the equation. Performing this operation, we get

[H2] = 1.19 M

You should verify that this is correct using your own calculator to confirm that you know how to do a cube root correctly.

? Exercise 13.3.2

The following reaction is at equilibrium:

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 \qquad (13.3.4)$$

The K_{eq} at a particular temperature is 13.7. If the equilibrium [N2] is 0.055 M and the equilibrium [H2] is 1.62 M, what is the equilibrium [NH3]?

Answer

1.79 M

The K_{eq} was defined earlier in terms of concentrations. For gas-phase reactions, the K_{eq} can also be defined in terms of the partial pressures of the reactants and products, P_i. For the gas-phase reaction

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$
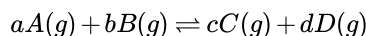
the pressure-based equilibrium constant, K_P, is defined as follows:

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

where P_A is the partial pressure of substance A at equilibrium in atmospheres, and so forth. As with the concentration-based equilibrium constant, the units are omitted when substituting into the expression for K_P.

✔ Example 13.3.3

What is the K_P for this reaction, given the equilibrium partial pressures of 0.664 atm for NO2 and 1.09 for N2O4?

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g) \qquad (13.3.5)$$

Solution

Write the K_P expression for this reaction:

$$K_P = \frac{P_{N_2O_4}}{P_{NO_2}^2}$$

Then substitute the equilibrium partial pressures into the expression and evaluate:

$$K_P = \frac{(1.09)}{(0.664)^2} = 2.47$$

? Exercise 13.3.3

What is the K_P for this reaction, given the equilibrium partial pressures of 0.44 atm for H_2, 0.22 atm for Cl_2, and 2.98 atm for HCl?

$$H_2 + Cl_2 \rightleftharpoons 2\,HCl \tag{13.3.6}$$

Answer

91.7

There is a simple relationship between K_{eq} (based on concentration units) and K_P (based on pressure units):

$$K_P = K_{eq} \cdot (RT)^{\Delta n}$$

where R is the ideal gas law constant (in units of L·atm/mol·K), T is the absolute temperature, and Δn is the change in the number of moles of gas in the balanced chemical equation, defined as $n_{gas,prods} - n_{gas,rcts}$. Note that this equation implies that if the number of moles of gas are the same in reactants and products, $K_{eq} = K_P$.

✔ Example 13.3.4

What is the K_P at 25°C for this reaction if the K_{eq} is 4.2×10^{-2}?

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 \tag{13.3.7}$$

Solution

Before we use the relevant equation, we need to do two things: convert the temperature to kelvins and determine Δn. Converting the temperature is easy:

$T = 25 + 273 = 298$ K

To determine the change in the number of moles of gas, take the number of moles of gaseous products and subtract the number of moles of gaseous reactants. There are 2 mol of gas as product and 4 mol of gas of reactant:

$\Delta n = 2 - 4 = -2$ mol

Note that Δn is negative. Now we can substitute into our equation, using $R = 0.08205$ L·atm/mol·K. The units are omitted for clarity:

$K_P = (4.2 \times 10^{-2})(0.08205)(298)^{-2}$
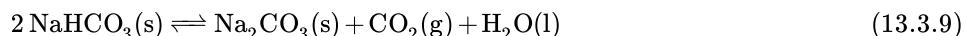
Solving,

$K_P = 7.0 \times 10^{-5}$

? Exercise 13.3.4 ·

What is the K_P at 25°C for this reaction if the K_{eq} is 98.3?,-

$$I_2(g) \rightleftharpoons 2\,I(g) \tag{13.3.8}$$

Answer

2.40×10^3

Finally, we recognize that many chemical reactions involve substances in the solid or liquid phases. For example, a particular chemical reaction is represented as follows:

$$2\,NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(l) \tag{13.3.9}$$

This chemical equation includes all three phases of matter. This kind of equilibrium is called a **heterogeneous equilibrium** because there is more than one phase present.

The rule for heterogeneous equilibria is as follows: *Do not include the concentrations of pure solids and pure liquids in* K_{eq} *expressions.* Only partial pressures for gas-phase substances or concentrations in solutions are included in the expressions of equilibrium constants. As such, the equilibrium constant expression for this reaction would simply be

$$K_P = P_{CO_2}$$

because the two solids and one liquid would not appear in the expression.

Key Takeaways

- Every chemical equilibrium can be characterized by an equilibrium constant, known as K_{eq}.
- The K_{eq} and K_P expressions are formulated as amounts of products divided by amounts of reactants; each amount (either a concentration or a pressure) is raised to the power of its coefficient in the balanced chemical equation.
- Solids and liquids do not appear in the expression for the equilibrium constant.